Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.

235741

LIBRARY
RECEIVED
★ SEP 25 1941 ★
U. S. Department of Agriculture

PRELIMINARY REPORT ON SUGARCANE WAX*

by
R. T. Balch,
Bureau of Agricultural Chemistry and Engineering
U. S. Department of Agriculture.

Upon the surface of sugarcane stalks there is deposited a layer of wax, the primary function of which is apparently to aid the plant in controlling the evaporation of moisture. Wax formation by plants of various types is very well known and the gathering of certain plant waxes has become a very important industry due to the demand for the waxes for use in polishes, industrial coatings and impregnating materials as well as in the making of phonograph records, crayons and many other articles.

The most important of these plant waxes is carnauba, obtained from the carnauba palm in Brazil. More than 14 million pounds[1] were imported in 1939. To supplement carnauba wax which can hardly meet the demand, Brazil has been steadily increasing its exports of ouricuri wax, which reached a figure of about 500,000 pounds[2] in 1940, most of which came to this country. Another very important plant wax is candelilla, obtained chiefly from northern Mexico although at various time some has been produced in southwestern Texas. The United States imported over 3-1/3 million pounds[3] of candellila wax from Mexico in 1939.

Among the principal commercial waxes not obtained directly from plants are beeswax, the various mineral waxes such as montan, ozokerite, ceresin, paraffin and a number of synthetic waxes. Many of these have been imported from Europe but due to the present war their supply has been practically shut off. This condition has caused some concern among wax users, particularly as the price of the other waxes has risen and, in the case of carnauba wax, very sharply.

During the World War of 1914 - 1918, there was established in Natal, South Africa, a new wax industry which used the discarded mud press-cake from the sugar factories as the source of their product - sugarcane wax. After considerable study, the mud press-cake was chosen because of its relatively high wax content and the apparent impracticability of obtaining it in quantity from the cane prior to milling or from the juice prior to clarification. It would be desirable to obtain it directly from the cane for it could then be obtained in much purer form. In the clarification of cane juice, the fats as well as the wax are trapped by the muds, so both of these are to be found in the crude wax product obtained by solvent extraction of the mud press-cake, which was the process used in Natal. There does not seem to be very much information available regarding the size to which the industry developed in Natal, but it is recorded[4] that some 12 million pounds of sugarcane wax were exported during 1924 and reported[5] that some had been received in this country. From information that has been gathered, it would appear that the Natal sugarcane wax had a number of objectionable characteristics such as a sticky feeling, a dark color which was difficult to bleach, and in some instances an objectionable odor[6]. The latter may have been due to the extraction of wax from press-cake which had been allowed to undergo putrefactive decomposition to reduce the fat content. At least it has been claimed that a harder wax could be obtained from fermented press-cake. The fatty substances are definitely responsible for the sticky feeling of the crude wax product and for a lowering of the melting point of the wax. Much of the color is also associated with the fatty fraction.

There has been a definite desire among wax users of this country to have [illegible] wax or one which might have specially desirable characteristics. This prompted the study of sugarcane wax by our Bureau which was carried on by C. A. Fort for the past three seasons and this year by the present writer. Fort has reported[6] upon the variation of cuticle wax as influenced by varieties and certain other factors, and upon the fat content of sugarcane. From his results it appears that, of all of the commercial varieties Co. 290 has the heaviest layer of wax; following in order are C.P. 28-19, 28-11, Co. 281, C.P. 29-320 and 29-116. The last-named variety has only about 1/8th the amount of wax as is on Co. 290 and would definitely be a very poor source of sugarcane wax. The melting point of the cuticle wax from different varieties of cane varied from 74 to 80° C.

Samples of this cuticle wax were submitted to the trade and elicited the opinion that this sugarcane wax did not have properties entirely comparable to those of carnauba wax, but that it would doubtless find a definite market if available in commercial quantities. The opinion was also expressed that the cuticle wax, although purer in composition, would have no greater value than the wax which could be obtained from the mud press-cake. This is a rather fortunate situation because of the difficulties that would be involved in obtaining the cuticle wax directly from cane stalks in quantity.

---

* Agricultural Chemical Research Division Contribution No. 22.

In order to obtain a better conception of the possibilities of recovering sugarcane wax from the mud press-cake as a by-product of the Louisiana cane sugar industry, an investigation was started this past season which has included a survey of the composition of mud press-cakes from different factories in respect to their wax content and a study of schemes for extracting and purifying the wax. So far, the work has been confined to laboratory operations.

In published reports of Natal operations, mud press-cake from Uba cane contained as high as 17% wax, and 14% was quite common. Burning the cane apparently lowered the wax content to less than 10%[8]. In Table I there are given the wax contents of Louisiana mud press-cakes, and it may be noted that the crude wax content ran as high as 17.7% and as low as 5.16%. It is believed that this wide difference cannot be ascribed to a difference of varieties alone, but is probably a result of a number of factors which have not been fully evaluated as yet. It is obvious that, for the most economical recovery of the wax, the wax content of the mud press-cake must be as high as it is possible to obtain, without adding any appreciable cost or difficulty to regular factory operations. The factors which may well influence the wax content of the muds are: varieties of cane, burning of the cane as an aid to harvesting, extraction efficiency of the mills, temperature of the maceration water, types of pumps with which the raw juice and the muds are handled, the type of clarification (including the equipment, temperature and pH control), and the manner in which the muds are handled from the clarifiers through the presses. It is easily conceivable that a large proportion of the wax may be lost by certain mud station practices. From the fact that one factory consistently produced a mud with a high content of wax while muds of others were so very much lower in wax it might be concluded that in this latter group there may be room for improvements in trapping the wax. Perhaps these may be considered as refinements to be studied after it has been demonstrated that a commercial wax can be recovered from the waste mud press-cake; so, work thus far has been confined mostly to a study of methods of wax extraction and purification in order to determine whether a product that meets commercial requirements could be obtained.

In considering various schemes for recovering wax from extraneous materials, solvent extraction appears to hold greatest promise from a commercial standpoint. As a basis for this statement, there is the widespread use of such methods in the oil and fat industry, and to a lesser extent in the wax industry itself. In order to apply such a method to mud press-cake, drying of the cake constitutes the first step in the process. It is not known at present how much moisture one can have with various possible solvents and yet obtain efficient extraction. Such a study is in progress, however, for it is important to know how much moisture must be evaporated from the cake, in order to keep the cost of drying as low as possible.

Wax is soluble in a number of available organic solvents, especially if they are warmed, and the selection of a suitable solvent will necessarily be based upon consideration of a number of factors. The approximate solubility of cuticle wax from Co. 290 cane in various commercial solvents is given in Table II. No attempt was made to determine the maximum solubility at elevated temperatures. The method of making these tests was to add 25 cc. of the solvent to 0.5 gram of the wax and then heat under a reflux condenser until equilibriu or complete solubility had taken place. Only [illegible] solvents would [illegible] dissolve the wax completely in the ratio of 2 g. per 100 ml. of solvent at their boiling point. It is to be noted too that the solubility of this wax exceeded 2 g. per 100 ml. of solvent at room temperature (approximately 23° C.) in only two solvents, which was determined by setting the solutions aside overnight in closed containers to allow the wax to crystallize to equilibrium, filtering of the solution and weighing the residue from a 10 ml. aliquot of the wax solutio after evaporation.

It has been suggested that the solvent for wax extraction should have a boiling point above the melting point of the wax. If this premise is accepte the selection of solvent is limited to a few of the solvents of the naphtha type, some of the chlorinated compounds, and coal tar products such as benzol, toluene, and xylene. Chlorinated compounds have the advantage of being less hazardous, but they are more expensive, higher in weight or density, and have the very unsatisfactory characteristic of hydrolyzing slightly with the formati of hydrochloric acid, thus requiring the use of acid-resistant extraction equi ment. The objection to the usual solvents put out by the petroleum industry is that the last traces are difficult to remove from the wax; if they remain in the wax, they interfere with the application of the wax for certain purposes. Toluene has been suggested as being the best solvent for wax extraction, even though its price is somewhat higher than some, since it meets the objections to some of the others. Price is not much of a consideration, since the loss of solvent can be kept low. For these reasons toluene has been used so far, for laboratory extraction work, in obtaining wax from mud press-cake.

The efficiency of extraction by any particular solvent is governed by several factors, of which moisture content has already been mentioned. Another factor which may be of considerable importance is the physical condition of the mud press-cake during extraction. Theoretically, highest extraction might be expected in a given time interval from finely divided material, but the handling of such material may create many problems that can be avoided if the cake is dried in a granular condition. In such physical condition, extraction by percolation or diffusion is possible rather than making a digestion and filtering the slurry of finely divided mud cake and wax solution. Laboratory experiments indicate that such a slurry is sometimes extremely difficult to filter and that excellent extraction can be achieved with hot toluene on mud that had been dried in a coarse granular condition and in which several consecutive extractions are made with the same solvent on the counter-current principle. Such a scheme, in comparision with the other methods, increases the wax content of that portion of solvent which is taken from the circuit and, hence requires less evaporation for the recovery of the wax. It is conceivable that equipment as elaborate as a beet-sugar diffusion battery might have very definite advantages for the extraction of wax from mud press-cake dried in suitable granular form, and it is planned to try out such a process and equipment on a pilot-plant scale. This would make the extraction process a continuous one, which would be desirable in large-scale operations.

The recovery of solvent from the spent cake and from the wax constitutes a major step in the process, because much of the cost of solvent extraction may arise from the loss of solvent. In some solvent-extraction processes, losses are frequently kept as low as 1/2% per cycle, and there is no reason to believe that similar results cannot be achieved in the extraction of wax from mud press-cake. For the recovery of solvent from the spent mud one has a choice of different methods, and a selection will depend upon what disposition is to be made of the dewaxed material. If it is desired to discard the spent muds, and moisture is of no consequence, steam distillation of the solvent would be satisfactory. Other systems, depending upon heating during agitation with or without vacuum, may be preferable in cases where it is desirable to have the spent material in a dry form for direct sale. As regards the spent mud press-cake, it doubtless has a distinct fertilizer value and can be sold at a price that should more than pay for the drying of the muds prior to the extraction of the wax. The average composition of the dewaxed muds has not yet been determined, but it is certain to be high in calcium phosphate.

The recovery of solvent from the wax solution consists simply of distilling off the solvent and blowing up the melted wax with steam or air to eliminate the last remnants of solvent. The same method holds for the recovery of the fat solvent from the fatty fraction and from the wax after removal of this fraction. After recovery, the solvents are ready for reuse directly unless it be found desirable to give them first some drying with a water adsorbent such as calcium chloride.

The crude wax extracted from the mud press-cake ranged in consistency from a relatively soft to a hard brittle product, depending upon the source. Referring back to Table I it can be noted that the fatty fraction in this crude wax varied from 17.6 to 42.2%, with an average of about 30%. There was a distinct correlation between the consistency of the crude wax and the proportion of the fatty fraction; those with the smaller amounts were hard and brittle. This lack of uniformity in the crude product from various sources strongly indicates the necessity of refining the wax, at least partially, before any attempt is made to place it on the market. Moreover, a great many wax users are not in a position to do any refining.

How much refining the original producer should do remains to be determined, but it is certain that the fatty fraction should be removed in order that the wax may have much more uniform composition and properties before reaching the market. It has been found that a fatty fraction can be removed from the wax by a diffusion process in the cold with a selective solvent. Referring to Table II, it can be noted that several of the solvents, notably the petroleum ethers, ethyl ether, and acetone, dissolve the cuticle wax to a very limited degree even at their boiling temperatures, but are excellent fat solvents. Of these solvents, acetone was chosen as having the greatest possibilities from the standpoint of initial cost and other considerations.

If the removal of the fatty fraction from the solid wax is to be carried out at air temperatures, the process is necessarily slow, requiring several days with several changes of solvent. The solvent can be used counter-currently upon the crude wax prepared in a coarse granular condition in order to reduce recovery expense and obtain a high concentration of fats in the solvent. The only equipment needed are tanks which can be closed to prevent evaporation of the solvent and from which the solution of fats can be pumped to any one of the other tanks holding the crude wax or to the evaporator for the recovery of the solvent from the fatty fraction. It has been found that the acetone-soluble fraction consists not only of the relatively low-melting point fats (around 30°) but also of a high melting point component (about 132° C.). This component gives the color reactions characteristic of sterols and its acetate derivative melts at 132°C. (uncorr.). It can thus be classified as a phytosterol.

The foregoing description of a process of wax extraction from mud press-cake can best be summarized by presenting the accompanying flow-diagram (Fig. I) which is based upon laboratory experience. It is planned to set up a pilot plant, embodying these features, at the Sugar Plant Field Station, Houma, La., for studying the principles of wax extraction and purification on a scale, which it is hoped, will permit a close approximation of the costs involved, as well as provide a supply of wax for large-scale tests by prospective users.

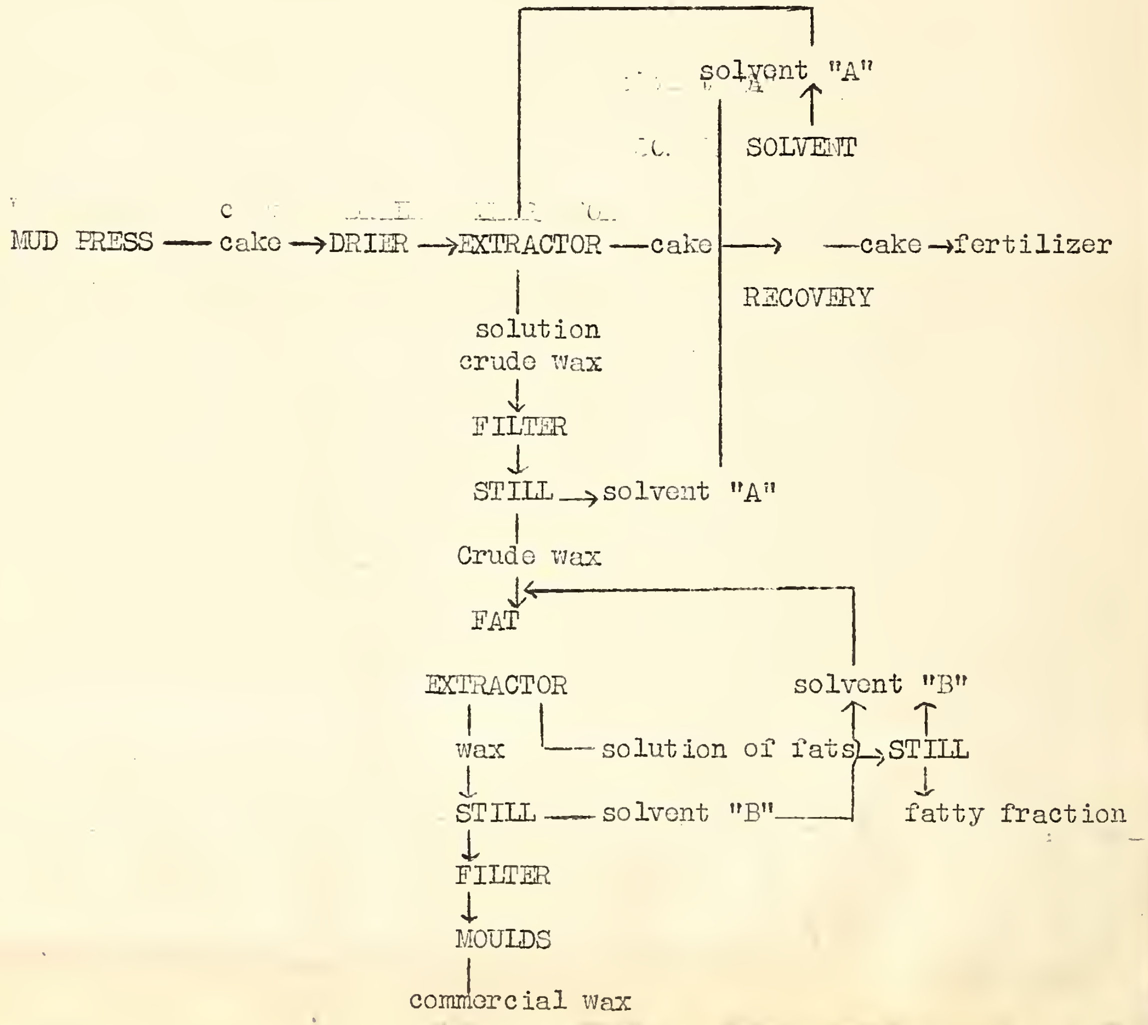

Fig. 1. FLOW DIAGRAM.

The opinion has also been expressed that the fatty fraction would have a commercial value if available in commercial quantities. If this should prove to be the situation, the total crude wax content can be used as a basis for determining the value of the mud press cake for by-products recovery.

References.
1. Agri. Statistics, U.S.Dept. Agri. 1940, p. 526.
2. Ind. & Eng. Chem. News Edition, 19, 410 (1941).
3. News Bull., Nat'l Farm Chem. Council, II, (5), p. 35, Mar. 10, 1941.

4. W. G. Cass, The So. Afri. Sugar Jour., 11, 271 (1927).
5. Personal communications.
6. Bull. Misc. Information #10, 1936. Issued by Royal Botanic Gardens, Kew, England.
7. C. A. Fort, The Sugar Bulletin, 17, no. 4, p. 41, Nov. 15, 1938.
   " " " 17, no. 20, pp. 3-4, Jul. 15, 1939.
8. Wm. Clacher, Int. Sugar Jour., 18, 22 (1916).

Table I. Wax Content of Louisiana Mud Press-Cakes. (Moisture-Free Basis)

Source of Mud Press-Cake Factory No.	Source of Mud Press-Cake Sample No.	Crude Wax (CCl$_4$-Extrn.)	Acetone Soluble Fraction On Sample	Acetone Soluble Fraction On Crude Wax	Wax Fraction (By Difference) On Sample	Wax Fraction (By Difference) On Crude Wax	Type of Mud Press	Remarks
		%	%	%	%	%		
1	1	17.68	6.01	33.7	11.67	66.3	Plate & Frame	Co 290 cane being milled
	2	15.29	5.27	34.5	10.02	65.5		
	3	15.27	4.37	28.6	10.90	71.4		
	4	7.50	2.43	32.3	5.07	67.7		Taken during clean up operations.
2	1	6.05	2.30	38.7	3.65	61.3	Do.	Obtained from dump*
3	1	12.38	3.73	30.1	8.65	69.9	Oliver-Campbell	
	2	9.83	2.22	22.6	7.61	77.4		
	3	9.31	1.64	17.6	7.67	83.4		
4	1	5.16	1.97	38.2	3.19	61.8	Do.	
	2	6.77	2.17	32.6	4.60	67.4		
5	1	7.40	2.73	36.9	4.67	63.1	Do.	
6	1	8.76	2.84	32.4	5.92	67.6	Pl. & Fr.	
7	1	7.99	2.71	33.9	5.28	66.1	Do.	
8	1	6.85	2.89	42.2	3.96	57.8	Oliver-Campbell	Co.281 cane being milled
9	1	8.15	2.54	31.2	5.61	68.8	Pl. & Fr	Obtained from dump*
10	1	14.24	3.35	23.5	10.89	76.5	Do.	Do.*
11	1	8.26	1.89	22.9	6.37	77.1	Oliver-Campbell	Do.*
Averages		9.82	3.00	30.5	6.82	69.5		

*Samples may not be representative, since flushing of muds to dump after pressing may partially dislodge wax from cake.

Table II. Solubility of Cuticle Wax (Co. 290) in Various Solvents.

Solvent	Boiling Point (Appx.)	Solubility of Cuticle Wax (Co. 290)	
		Room Temp.	Boiling
	°C.	g/100 cc.	
Skelly-solve "F"	35-59	-	<2
"B"	63-70	0.67	>2
"C"	89-98	0.71	>2
Shell 8206	60-82	0.82	>2
8182	116-139	0.73	>2
8196	96-114	0.78	2
8215	27-32	-	>2
Neville-Benzol	78-82	1.06	2
Std. Oil - Naphtha	93	0.73	>2
Phillips n-Pentane	33	-	<2
iso- "	27	-	<2
Hexane	57	0.61	2
1,2 Dichlorethylene	48	>2.0	>2
Methylene Chloride	40	-	<2
Cyclohexane	81	1.30	>2
Methyl Hexane	100	0.95	>2
Dioxane	99	0.29	>2
Isopropyl ether	64	0.52	>2
Ethylene Dichloride	83	0.60	>2
Perchlorethylene	119	0.86	>2
1,1,2,2 Tetrachlorethane	136	0.87	>2
Trichlorethylene	79	>2.0	>2
N-Butyl Chloride	78	1.17	>2
Nitro Ethane	110	Gel	>2
Nitro Methane	101	Gel	<2
Ethanol (95%)	78	Gel	<2
Carbon Tetrachloride	77	1.24	>2
Benzol	80	1.04	>2
Toluene	111	1.43	>2
Acetone	56	0.11	<2
Ethyl Ether	35	-	<2